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Selective removal of H₂S from sour gases with microporous membranes. Part II. A liquid membrane of water-free tertiary amines

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Abstract

In the present study the application of a liquid membrane for selective removal of H₂S from gases also containing CO₂ was investigated. The liquid membrane was filled with pure methyl-di-ethanol-amine (MDEA). A theoretical model was developed to describe (a) the chemical equilibrium between the dissolved gas and MDEA in the membrane and (b) the physical equilibrium between the solute (CO₂ and H₂S) in the gas and the liquid phase. Experimentally H₂S and CO₂ fluxes were determined in a setup consisting of two well mixed gas phase compartments separated by a flat liquid membrane. The fluxes were interpreted with the theoretical model and separately measured physical constants (solubility, diffusivity and the porosity/tortuosity factor of the membrane material). No reaction of CO₂ with MDEA was observed which is attributed to the absence of water. A weak acid/base interaction of H₂S and MDEA was found to increase the H₂S transport through the membrane which includes higher selectivity. This effect is more pronounced at lower partial pressures of H₂S.

Key words: gas separations, microporous membranes, H₂S/CO₂ selectivity

1. Introduction

In Part I of this study [1] porous membranes were used to separate a gas and liquid phase in a gas absorption process and to improve the selective H₂S removal. In this part an alternative application of membranes in a selective H₂S removal process is studied: a liquid membrane, i.e. a porous membrane impregnated with alkanolamines acting as a selective carrier.

From the different alkanolamines available

(primary, secondary and tertiary) the highest selectivity for H₂S is reached with aqueous solutions of tertiary alkanolamines because the reaction rate of these amines with CO₂ is the lowest compared to the rates with primary or secondary amines. The reaction rate of H₂S with these amines can be considered as instantaneous in relation to mass transfer.

Several authors, e.g. Donaldson and Nguyen [2], Barth et al [3,4] and Versteeg and Van Swaaij [5], studied the mechanism of the reaction between CO₂ and tertiary amines. It is concluded that due to the N-atom in the amine, which does not have a free hydrogen atom, no carbamate ions can be formed contrary to the

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reaction with primary and secondary amines. However, in the presence of water hydration of CO_2 occurs resulting in bicarbonate and protonated tertiary alkanolamines. A net reaction of CO_2 and the amine is the result.

According to the reaction mechanism in water-free tertiary amines, CO_2 dissolves only physically while H_2S still reacts with the amine and therefore the H_2S flux can be enhanced by the chemical reaction. Unfortunately, most of the tertiary alkanol amines that are liquids at room temperature have fairly high viscosities, i.e. the viscosity of methyl-di-ethanol-amine (MDEA) is 8×10^{-2} Pa-sec at 298 K. This substantially complicates their use in the conventional absorption processes.

In the present study the application of a supported liquid membrane is investigated. A liquid membrane acts simultaneously as ab- and desorber when it is placed between two gas phases while a stagnant liquid (e.g. MDEA) is present in the pores of the membrane. This liquid should selectively absorb one of the gas components. The selectivity and the flux can be enhanced further by adding a carrier to the membrane liquid which reacts reversibly with this gas component. The reaction product and the dissolved gas diffuse to the low concentration side of the membrane.

For this type of separation processes only a few systems have proven their applicability: sour gas purification by aqueous alkaline and amine solutions, alkene separation from mixtures with alkanes by solutions of silver ions and oxygen separation from air by transport with metalcomplexes. These systems are reviewed by Matson et al. [6] and Way et al. [7].

The incorporation of supported liquid membranes in hollow fibre membrane modules offers the opportunity to create a compact mass transfer apparatus. This configuration is already used for gas separations with dense polymeric membranes [6]. Bhave and Sirkar [8] showed that it can also be used for supported

liquid membranes. Majumdar et al. [9] showed that the hollow fibre module configuration can also be used with the liquid membrane in the shell side of a membrane module containing two kinds of fibres. One part of the fibres is used for the feed gas while the other part is used for the sweep gas. When these fibres are stacked very close the resulting small liquid film in between can be considered as the liquid membrane allowing the transfer of gas components.

A liquid membrane for selective H_2S removal from coal gas which also contains CO_2 is reported by Matson et al. [10], who used a carbonate/bicarbonate solution in staged liquid membranes. Between two layers of liquid membrane they applied a spacer filled with inert gas. Such a system offers a stronger barrier for the CO_2 flux than for the H_2S flux, this increasing the selectivity for H_2S . The industrial application of such a membrane unit is very difficult because of the construction of the module. Besides, a major drawback of most liquid membranes in gas separations is the instability of the membrane which is caused by the evaporation of (part of) the liquid from the membrane.

Generally pure tertiary alkanolamines have extremely low vapour pressures. Therefore it can be assumed that the instability problem will be reduced when the pure amines are used instead of their aqueous solutions. In the present study the chemical and physical aspects of a liquid membrane consisting of pure tertiary alkanol amines are investigated for the selective removal of H_2S from gases which also contain CO_2 . The applicability of a liquid MDEA membrane for the selective removal of H_2S is actually tested.

2. Theory

In membrane literature the system of a gas diffusing through a liquid layer in which also a reaction takes place is referred to as facilitated

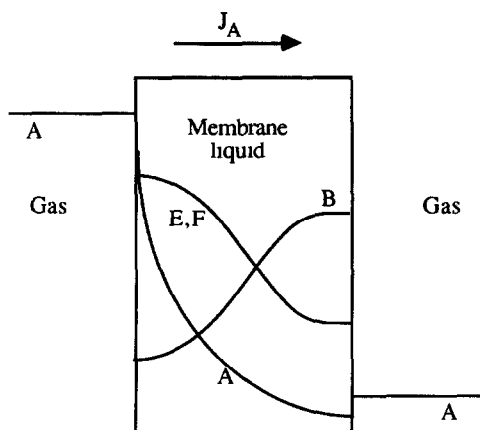
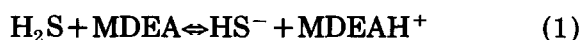


Fig 1 Concentration profiles in a liquid membrane system with facilitated transport Equilibrium reaction $A + B \rightleftharpoons E + F$

transport. Such a membrane is presented schematically in Fig. 1, based on the simple reversible reaction: $A + B \rightleftharpoons E + F$. Due to the reaction of the dissolved gas (A) and the so-called carrier molecule (B) product gradients (E and F) are present which form an extra way of transporting A through the layer. At the low concentration side E and F combine again to give B which diffuses back to the side with the high concentration of A while A is released to the gas phase at the low concentration side of the membrane.

In the present study the enhancement of the H_2S transport is carried out according to the reaction:



For the mathematical description of this system the following general equation is used:



From the differential mass balances the concentration profiles of the components can be calculated:

$$D_A \frac{d^2 C_A}{dx^2} = k_1 C_A C_B - k_{-1} C_E C_F \quad (3)$$

$$D_B \frac{d^2 C_B}{dx^2} = k_1 C_A C_B - k_{-1} C_E C_F \quad (4)$$

$$D_E \frac{d^2 C_E}{dx^2} = k_{-1} C_E C_F - k_1 C_A C_B \quad (5)$$

$$D_F \frac{d^2 C_F}{dx^2} = k_{-1} C_E C_F - k_1 C_A C_B \quad (6)$$

with boundary conditions:

$$x=0,$$

$$C_A = C_{A0}$$

$$\frac{dC_B}{dx} = \frac{dC_E}{dx} = \frac{dC_F}{dx} = 0 \quad (7)$$

$$x=\delta,$$

$$C_A = C_{A\delta}$$

$$\frac{dC_B}{dx} = \frac{dC_E}{dx} = \frac{dC_F}{dx} = 0 \quad (8)$$

The boundary conditions of B, E and F represent the fact that B, E and F are non-volatile and stay within the membrane.

Methods of solving the equations are reported by several authors, see e.g. Ward [11], Smith et al. [12], Smith and Quinn [13] and Kemena et al. [14]. From the concentration profiles the flux through the membrane can be calculated. The influence of the chemical reaction on the flux can be expressed as the enhancement or facilitation factor, which is the ratio of the flux with and without the reaction taking place for conditions with identical concentration differences.

Generally diffusion in a supported liquid membrane is slow compared to the chemical reaction. Therefore the reaction can be considered as instantaneous at equilibrium at each place in the membrane. By assuming a concentration difference over the membrane the facilitation factor can be calculated as a function of the equilibrium constant analogous to the approach followed by Olander [15]. The overall flux of A is expressed as:

$$J_A = -D_A \frac{dC_A}{dx} - D_E \frac{dC_E}{dx} \quad (9)$$

which is solved with the boundary conditions to give:

$$J_A = -\frac{D_A}{\delta} (C_{A,0} - C_{A,\delta}) - \frac{D_E}{\delta} (C_{E,0} - C_{E,\delta}) \quad (10)$$

The facilitation factor, Φ , is the ratio of J_A and the physical flux:

$$\Phi = 1 + \frac{D_E}{D_A} \frac{C_{E,0} - C_{E,\delta}}{C_{A,0} - C_{A,\delta}} \quad (11)$$

$C_{E,0}$ and $C_{E,\delta}$ can be calculated from $C_{E,0}$ and $C_{E,\delta}$ resp., the equilibrium constant and the total concentration of amine, C_{Btot} . The stoichiometry of reactions (1) and (2) gives the condition $C_E = C_F$. This yields the quadratic equation:

$$K = \frac{C_E C_F}{C_A C_B} = \frac{C_E^2}{C_A (C_{Btot} - C_E)} \quad (12)$$

Figure 2 shows that the facilitation factor goes through a maximum when the equilibrium constant is increased. At low values of the equilib-

rium constant hardly any products are formed to give a facilitated flux. At high values of the equilibrium constant the formed products hardly combine again at the low pressure side to release the transferred gas.

In Part I of this study selectivity was expressed as the ratio of the fluxes of H_2S and CO_2 each divided by the concentration differences over the mass transfer film. For the facilitated membrane in which only the H_2S flux is enhanced by the chemical reaction this selectivity is equal to the facilitation factor of H_2S when it is multiplied with the ratio of the diffusivity and the distribution coefficients of H_2S and CO_2 :

$$S = \frac{J_{H_2S} / (C_{H_2S,HP} - C_{H_2S,LP})}{J_{CO_2} / (C_{CO_2,HP} - C_{CO_2,LP})} = \frac{m_{H_2S}}{m_{CO_2}} \frac{D_{H_2S}}{D_{CO_2}} \Phi \quad (13)$$

Because the ratio of the diffusion and distribution coefficients are physical constants, Fig. 2 can also be regarded as an illustration for the H_2S selectivity as a function of the equilibrium constant.

For the interpretation of experimentally de-

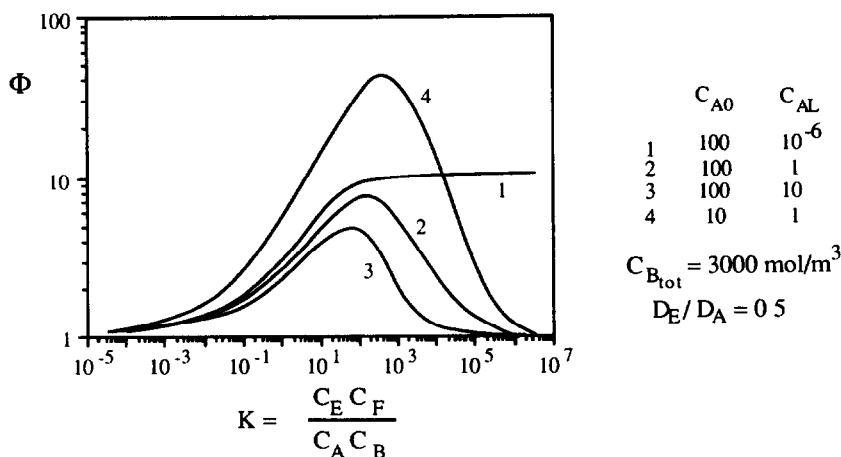


Fig. 2 Facilitation factor as a function of equilibrium constant and transmembrane concentration difference for the equilibrium reaction $A + B \rightleftharpoons E + F$

terminated fluxes in terms of selectivity and facilitation factors, the solubility and diffusion coefficients of CO₂ and H₂S in the membrane liquid, pure MDEA, are needed. These are not available in the open literature and therefore these values are determined experimentally in the present study.

The physical solubility and diffusion coefficient of CO₂ in aqueous solutions of alkanolamines cannot be measured directly because CO₂ reacts directly with the amines. Nitrous oxide is an inert gas which is very similar to CO₂ in many physical properties (Table 1). It was found that CO₂ and N₂O behave similar in non-reacting low viscosity liquids [16]. Therefore, from the diffusion and distribution (solubility) coefficient of N₂O these values can be estimated for CO₂. In the present study it will be investigated whether this also holds for the non-aqueous amines.

The diffusion coefficients used above to describe mass transfer in the membrane are the so-called effective diffusion coefficients. They are related to the binary diffusion coefficient according to eqn. [14].

$$D = D_{ij} \frac{\epsilon}{\tau} \quad (14)$$

The porosity/tortuosity factor, ϵ/τ , depends on the geometry of the membrane [17]. For simple geometries of pores ϵ/τ can be calculated theoretically, however, for most practical porous structures this factor must be determined experimentally.

TABLE 1

Physical data of the absorbing gases

| | N ₂ O | CO ₂ | H ₂ S |
|----------------------------|------------------|-----------------|------------------|
| <i>M</i> (g/mol) | 44.01 | 44.01 | 34.08 |
| <i>T_c</i> (°C) | 36.5 | 31 | 100.4 |
| <i>P_c</i> (atm) | 71.7 | 72.9 | 81.9 |
| <i>μ</i> (D) | 0.167 | 0 | 0.97 |

3. Experiments

3.1. Solubility

Solubility of a gas phase component in a liquid phase in which the solute also reacts chemically can be expressed as in eqn. (15). As an example the dissociation of H₂S with an amine (eqn. 1) is taken:

$$m_{\text{tot}} = m_{\text{phys}} + m_{\text{chem}} = \frac{C_{\text{H}_2\text{S,L}}}{C_{\text{H}_2\text{S,G}}} + \frac{C_{\text{HS}^-\text{,L}}}{C_{\text{H}_2\text{S,G}}} \quad (15)$$

The equilibrium constant relates [H₂S]_L and [HS[−]]_L similar to eqn. (12).

To determine m_{tot} , equilibrium measurements were performed in two different set-ups. The first consisted of a stirred gas–liquid cell operated batch wise as described by Versteeg et al. [18]. The liquid was led into this cell after which the gas phase was evacuated. Next the gas/liquid equilibrium was allowed to establish. One of the gases, e.g. CO₂, N₂O or H₂S was fed to the cell to an initial pressure (P_0) after which the stirrer was started. The pressure was monitored with an electronic pressure transducer until equilibrium was reached (P_∞). The distribution coefficient, m_{tot} , can be calculated according to eqn. (16).

$$m_{\text{tot}} = \frac{C_L}{C_G} = \frac{P_0 - P_\infty}{P_\infty} \frac{V_G}{V_L} \quad (16)$$

This method was not accurate enough for the absorption of CO₂ and H₂S in MDEA because the pressure at equilibrium was very low compared to the initial pressure which affects the accuracy of eqn. (15) substantially. Therefore, in the second set-up a gas was led continuously via a sintered glass plate through a small-scale bubble column filled with MDEA. Liquid samples could be taken and these were analysed by titration for the content of the acidic gases. In

these experiments the gas solubility at atmospheric pressures was measured.

Totally water free liquids could not be obtained either by long time exposure to deep vacuum or standing on molecular sieves. The lowest water content that could be achieved during the experiments was around 0.1 wt.%.

3.2. Diffusion coefficient

The determination of diffusion coefficients from absorption experiments in a laminar film reactor is a widely used method because the interfacial area and the hydrodynamics of the liquid phase are known, see e.g. Nijssing et al. [19] and Bird et al. [20]. From the experiments the product of solubility and the square root of the diffusion coefficient can be derived. The solubility was measured separately (section 3.1) in order to be able to calculate the diffusion coefficient.

3.3. Permeation experiments

The fluxes through the liquid membrane were measured in a stationary operated stirred cell (Fig. 3). The gas flows and concentrations were measured in order to calculate the fluxes. Gas flows were measured with a soap film meter and

the concentrations were measured with a gas chromatograph, Varian 3400, equipped with a thermal conductivity meter (TCD) and a flame photometric detector (FPD) for the low ppm range of H_2S . All the experiments were carried out at atmospheric pressure. To study the effect of the presence of CO_2 on the H_2S flux and *vice versa*, fluxes were measured with mixtures of CO_2 or H_2S with nitrogen in balance.

The membranes were purchased from Pall, and had a thickness of 100 μm and a mean pore diameter of 0.1 μm . These membranes made of polyamide easily held MDEA in their pores.

The determination of the ϵ/τ factor (eqn. 14) was carried out with the diffusion of CO_2 through a water filled membrane. One gas chamber was filled with pure CO_2 and closed while the other gas chamber was swept with nitrogen. Pressure decrease in the CO_2 chamber and the CO_2 content in the nitrogen stream were measured to calculate the mass transfer coefficient in the membrane. With the diffusion coefficients of these two gases in water, the ϵ/τ factor was calculated from the measured mass transfer coefficient

$$J = k_m \Delta C = \frac{D_v \epsilon}{\delta \tau} \Delta C \quad (17)$$

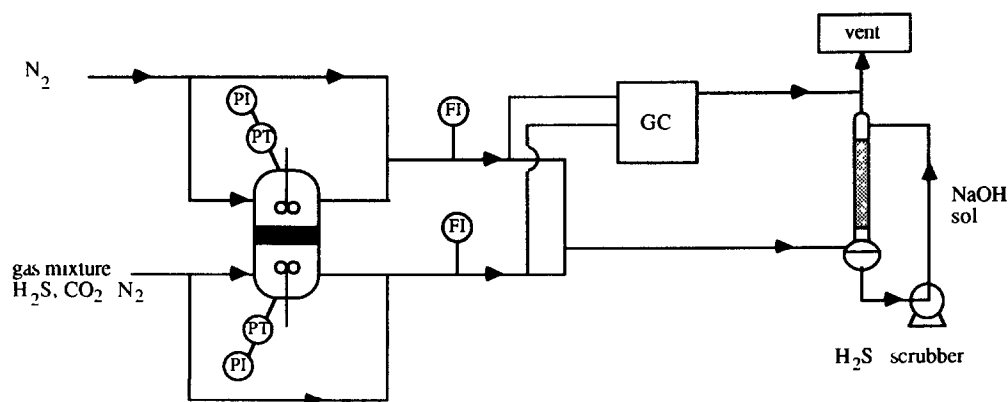


Fig 3 Experimental set-up Stirred cell with liquid membrane

4. Results

4.1. Solubility

The experimentally obtained distribution coefficients of N_2O in MDEA/water mixtures at 298 K are presented in Fig. 4. Initially with an increasing MDEA content the N_2O solubility decreases, but from a MDEA mole fraction of 15%, solubility increases again. The same phenomena were measured by Versteeg and Oyeveaar [21] in DEA/water mixtures and Littel et al. [22] using aqueous solutions of triethanolamine and diethylmonoethanolamine. In Fig. 4 also the solubility predicted by the ideal mixing rule [23] is given:

$$\ln m_{\text{mix}} = \sum y_i \ln m_i \quad (18)$$

It is clear from Fig. 4 that the system MDEA/ H_2O/N_2O is a non-ideal one. The solubility of CO_2 in pure MDEA, $m_{CO_2} = 4.4$, was found to be much higher than that in pure water ($m = 0.85$). Even if it is assumed that the residual small amount of water present in the amine reacts completely with CO_2 , the total solubility is still higher. The ratio of CO_2/N_2O solubility is 1.360, while in pure MDEA the ratio is 3.4. Therefore it must be concluded that the $CO_2/$

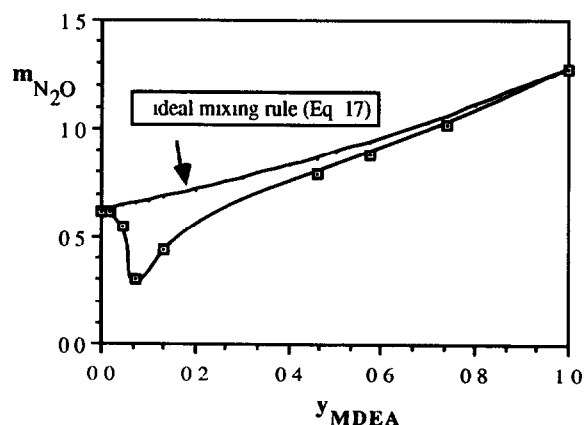


Fig. 4 Distribution coefficient of N_2O in MDEA/ H_2O mixtures, $T = 298$ K. Comparison with ideal mixing rule

N_2O analogy for prediction of the CO_2 solubility cannot be used over the whole composition range of the water/MDEA mixtures.

To see whether the high solubility of CO_2 in MDEA can be attributed to a specific group in the MDEA molecule the solubility of CO_2 in other alkanolamine-like solvents was measured. Firstly, the influence of the number of hydroxyl groups in the amine was investigated. In an experimental series starting with triethylamine other solvents were chosen in which the ethyl groups were replaced with ethanol groups up to triethanolamine. The same comparison can be made between methyldiethylamine and methyldiethanolamine. Secondly, the influence of the N-atom in the amines was compared to similar solvents in which the N-atom was replaced by a C-H group. Comparison was made between the solubilities in 3-methylpentane and methyldiethylamine. The same was done with 3-methyl-1,5-pentanediol and methyldiethanolamine. The results are presented in Table 2. In each of the three groups the solubility of N_2O decreases when more hydroxyl groups are present. Changing a C-H group for a N-atom does not affect the N_2O solubility significantly. Introducing more hydroxyl groups in the various amines increases both CO_2 and H_2S solubility, with the exception of triethanolamine which has lower solubilities than ethyldiethanolamine. The ratio of H_2S and CO_2 solubilities (selectivity) does not show a consistent relation with the number of hydroxyl groups in the amines and the variation of this ratio does not reveal a specific super H_2S selective liquid. When the N-atom is replaced by a C-H group the solubilities of all three gases decreased. Obviously the N-atom with its uncoupled electron pair is not as inert as a C-atom without free electrons. This is certainly needed for the acid-base reaction between the amine and H_2S .

From these observations it must be concluded that the presence of hydroxyl groups in-

TABLE 2

Solubilities of N₂O, CO₂ and H₂S in various solvents at 298 K

| Solvent | $m_{\text{N}_2\text{O}}$ | m_{CO_2} | $m_{\text{H}_2\text{S}}$ | $m_{\text{CO}_2}/m_{\text{N}_2\text{O}}$ | $m_{\text{H}_2\text{S}}/m_{\text{CO}_2}$ |
|--------------------------|--------------------------|-------------------|--------------------------|--|--|
| Water | 0.62 | 0.85 | 2.5 | 1.4 | 2.9 |
| Triethylamine | 3.6 | 3.0 | 14 | 0.83 | 4.7 |
| Diethylmonoethanolamine | 2.7 | 4.8 | 30 | 1.8 | 6.3 |
| Ethyl-diethanolamine | 1.6 | 2.3 | 74 | 1.4 | 3.2 |
| Triethanolamine | 0.9 | 7.3 | 53 | 8.1 | 7.3 |
| Methyldiethylamine | 4.2 | 4.2 | 22 | 1.0 | 5.2 |
| Methyldiethanolamine | 1.3 | 4.4 | 25 | 3.4 | 5.7 |
| 3-Methylpentane | 3.5 | 2.0 | 5.9 | 0.57 | 3.0 |
| 3-Methyl-1,5-pentanediol | 1.3 | 1.0 | 5.9 | 0.77 | 5.9 |

creases the solubility of both CO₂ and H₂S but that no drastic selectivity changes can be expected. The N-atom in the amines is needed to guarantee a significant solubility for H₂S but it also seems to influence the CO₂ solubility in the same direction.

4.2 Diffusion coefficient

The diffusion coefficients of N₂O in pure MDEA and two solutions with small quantities of water added (5 and 10 mol%) were determined in a falling film reactor (wetted wall column). The experimental result is the product of the distribution coefficient and the square root of the diffusion coefficient: $m\sqrt{D}$. When the distribution coefficient is taken from section 4.1, the diffusion coefficient can be calculated. The data are presented in Fig. 5 as a function of solvent viscosity. This figure also contains the data obtained by Versteeg and van Swaaij [24] for aqueous solutions of MDEA, up to a concentration of 2200 mol/m³. A fit of both sets of data to a modified Stokes–Einstein relation ($D\eta^\alpha = \text{constant}$) gives $\alpha = 0.53$. Generally, for large variations in viscosity, α is found in a range between 0.5 and 1, depending on the combination of solvent and solute [23].

4.3 Permeation experiments

To determine the porosity/tortuosity factor of the membrane, CO₂ diffusion through a water filled membrane was measured. The gas streams needed humidification to prevent evaporation of water from the membrane. With the diffusion coefficient of CO₂ in water at 298 K of 1.92×10^{-9} m²/sec the ϵ/τ factor was calculated to be 0.2 which is in agreement with the experimental results in Part I [1] and a previous study [17].

4.4 Selectivity

The fluxes measured with CO₂ and H₂S are presented in Figs. 6 and 7. From these data it can be concluded that the CO₂ flux is not influenced by the presence of H₂S and *vice versa*.

In Part I of this study [1], it was found that the presence of CO₂ reduces the H₂S flux. This was explained by the competition between CO₂ and H₂S to react with the aqueous amine. This is not the case for the liquid membrane as is shown in Fig. 6. The CO₂ flux shows a linear dependancy with the CO₂ concentration which indicates that no chemical reaction is involved. Since MDEA is a tertiary amine and water is

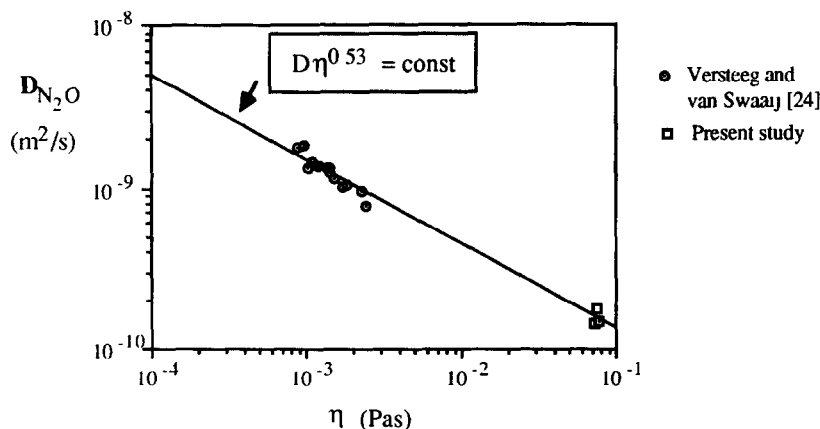


Fig 5 Diffusion coefficient of N_2O as a function of liquid viscosity in MDEA/ H_2O mixtures, $T=298\text{ K}$. Correlation of data with a modified Stokes-Einstein relation

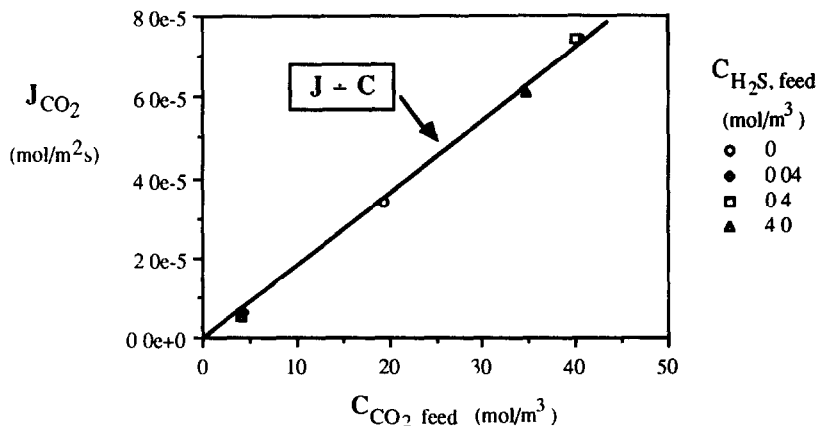


Fig 6 CO_2 flux as a function of the CO_2 and H_2S gas phase concentrations at the feed side of a supported liquid MDEA membrane (room temperature, atmospheric pressure)

not present, this was expected. According to eqn. (17), the slope in Fig. 6 which is 1.7×10^{-6} m/sec, can also be calculated from the experimentally determined solubility, diffusion coefficient and the ϵ/τ factor if the downstream concentration of CO_2 is neglected. This is a reasonable assumption since the relative maximum partial pressure at the downstream side was about 2% of the partial pressure at the upstream side. The theoretical value of the slope (1.3×10^{-6} m/sec) is comparable to the value obtained for the slope in Fig. 6 (1.7×10^{-6} m/sec). The difference (20%) between these two

values must be attributed to the experimental inaccuracy of the data for solubility, diffusivity and ϵ/τ . For the diffusivity of CO_2 the measured value of N_2O was taken, which is correct if it is assumed that only the molecular weight determines diffusivity [23].

The experimentally determined H_2S fluxes are presented in Fig. 7. The slope in this figure is 0.85, indicating an influence of the chemical reaction. This phenomenon can be interpreted in terms of the equilibrium constant (Fig. 2). However, the physical solubility coefficient must be known to relate the liquid phase con-

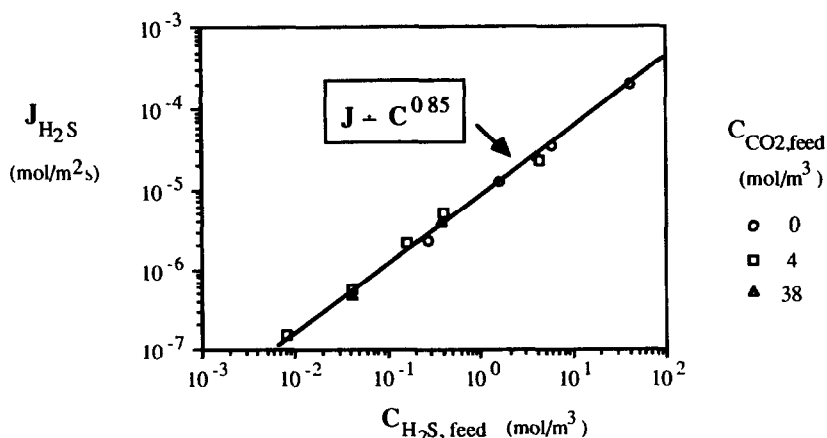


Fig 7 H_2S flux as a function of the H_2S and CO_2 gas phase concentrations at the feed side of a supported liquid MDEA membrane (room temperature, atmospheric pressure).

centration of H_2S to the measured gas phase concentration (eqn. 12).

If it is assumed that diffusion coefficients, ϵ/τ factor and the membrane thickness are known, eqn. (10) relates experimental data ($J_{\text{H}_2\text{S}}$, $\text{H}_2\text{S}_{\text{HP}}$, $\text{H}_2\text{S}_{\text{LP}}$) to m_{phys} and K . Equation (15) relates the measured total solubility (Table 2) to m_{phys} and K . From these two independent relations m_{phys} and K were fitted by trial and error. The result shows a small degree of dissociation of H_2S ($K=2 \times 10^{-4}$) and a relatively high physical solubility of H_2S in the pure MDEA, $m_{\text{phys}}=24$. The small equilibrium constant indicates that in MDEA dissociation of molecules into ionic species hardly occurs. If a co-solvent can be found which, when mixed with MDEA, has a better capability of allowing ionic species, an even more H_2S selective solvent would be obtained. With the fitted values of m_{phys} and K facilitation factors of 1 to 2.2 are obtained (eqn. 11). The calculated and the experimentally obtained H_2S fluxes are compared in the parity plot of Fig. 8 showing a reasonable good fit.

The H_2S and CO_2 fluxes that were obtained in the simultaneous absorption experiments give experimental selectivities. The data show an increase of selectivity with lower partial

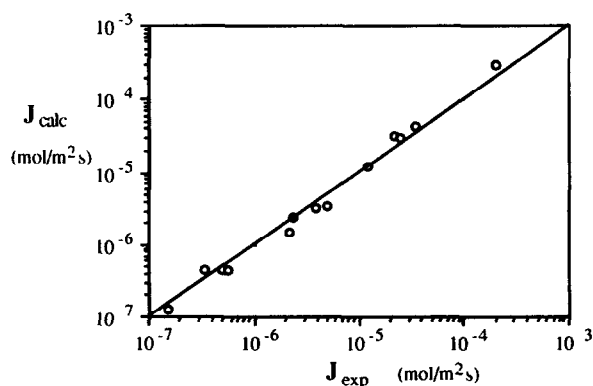


Fig. 8 Parity plot of calculated versus experimental H_2S fluxes in a supported liquid MDEA membrane. Calculation parameters: $m_{\text{phys},\text{H}_2\text{S}} = 24$, $K = 2 \times 10^{-4}$ (eqn. 1)

pressures of H_2S which is due to an increase of the facilitation. This effect is also shown in Fig. 2 where lines number 3 and 4 have the same ratio of driving force over the membrane but the case with the lower concentrations (line 4) gains most from the facilitation.

Equation (13) predicts selectivity on the basis of the facilitation factor for H_2S . A parity plot, Fig. 9, compares the experimental selectivity values with those derived theoretically (the ratio of diffusivities is taken as 1). Although the correlation is not very accurate, Fig.

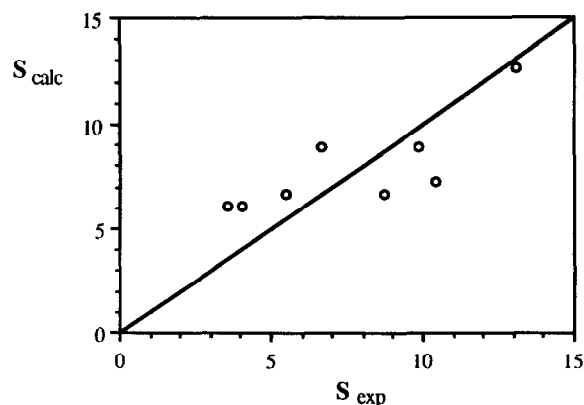


Fig. 9 Parity plot of calculated versus experimental H_2S selectivity using a supported liquid MDEA membrane. Calculation parameters $m_{phys,CO_2} = 4.4$, $m_{phys,H_2S} = 24$, $K = 2 \times 10^{-4}$ (eqn. 1).

9 shows that the trend in selectivity is rather well predicted with eqns. (11) and (13).

5. Conclusions

In the present study the application of a liquid membrane for selective removal of H_2S from gases also containing CO_2 was investigated. The liquid membrane was filled with pure MDEA which showed no reaction with CO_2 . To a limited degree, reaction was observed between H_2S and the amine ($K = 2 \times 10^{-4}$) which results in a higher selectivity than can be expected on the basis of the physical solubility of CO_2 ($m_{phys} = 4.4$) and H_2S ($m_{phys} = 24$). As expected from theory this so-called facilitation of H_2S is more pronounced at lower partial pressures of H_2S .

To further increase H_2S selectivity one could aim for a solvent with a higher H_2S solubility or a combination of tertiary amine and a co-solvent which allows a further dissociation of the physically dissolved H_2S .

In the case of pure MDEA as absorption liquid the analogy between the solubility of N_2O and CO_2 [16] is not valid like for aqueous solutions of alkanolamines. The solubility of N_2O

in MDEA/ H_2O mixtures was shown to be very non-ideal. It goes through a minimum when MDEA content is increased starting from pure water. The ideal mixing rule for solubility of gases in mixtures of liquids cannot be applied to predict the solubility.

The solubility of CO_2 and H_2S was tested in 8 organic liquids, i.e. amines, alkanolamines, alkanes and alkanols. Two liquids were studied in which the N-atom was replaced by a C-H group. The presence of the N-atom in the (alkanol-)amines gives higher solubilities of CO_2 and H_2S in comparison with similar alkanes and alkanols. Increasing the number of hydroxyl groups in alkanolamines also seems to increase solubility. However the ratio of H_2S/CO_2 solubility is not influenced significantly by the presence of the N-atom or the hydroxyl groups.

The diffusivity of N_2O in pure MDEA and MDEA mixed with small quantities of water was determined experimentally in a laminar film reactor. These data plus data from literature on diffusivity of N_2O in aqueous solutions of MDEA [24] can be correlated with a modified Stokes-Einstein equation, $D \eta^{0.53} = \text{constant}$.

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List of symbols

| | |
|-------|--|
| C | concentration (mol/m ³) |
| D | diffusion coefficient (m ² /sec) |
| J | flux (mol/m ² -sec) |
| k_m | mass transfer coefficient (m/sec) |
| k_1 | forward reaction rate constant [m ³ /(mol-sec)] |

| | |
|------------|--|
| k_{-1} | backward reaction rate constant [m ³ /(mol·sec)] |
| K | equilibrium constant (–) |
| m | distribution coefficient C_L/C_G (–) |
| M | molar weight (g/mol) |
| S | selectivity (eqn. 13) (–) |
| T | temperature (°C) |
| P | pressure (atm) |
| V | volume (m ³) |
| x | coordinate in membrane thickness (m) |
| y | mole fraction (–) |
| ΔC | concentration difference (mol/m ³) |
| δ | membrane thickness (m) |
| ϵ | membrane porosity (–) |
| η | dynamic viscosity (Pa·sec) |
| Φ | facilitation/enhancement factor (eqn. 11) (–) |
| μ | dipole moment (D) |
| τ | membrane tortuosity |

Indices

| | |
|----------|--|
| c | critical value |
| G | gas phase |
| HP | high pressure side, gas phase |
| L | liquid phase |
| LP | low pressure side, gas phase |
| 0 | location in membrane, high pressure side |
| δ | location in membrane, low pressure side |
| tot | total |
| phys | physical |
| chem | chemical |

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